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LOW TEMPERATURE THERMOELECTRIC POWER OF (SN)X,(U)
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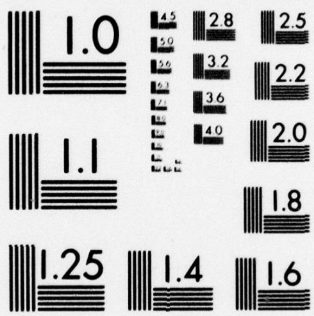

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6 Low Temperature Thermoelectric Power of $(SN)_x$

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The Thermoelectricpower of $(SN)_x$ has been studied from 0.1K to 4.2K. Above 1K a large phonon drag contribution is found, this can be associated with strong phonon-electron scattering. The superconducting transition is observed as is an increasing thermopower below 1K which can be associated with a Kondo effect. An interesting magnetic field behaviour is observed both above and below T_c.

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Polysevic sulfur nitride, $(SN)_x$, is an unusual material from several aspects. Crystals are formed by the solid state polymerization of S_aN_2 and consist of bundles of $(SN)_x$ fibers with diameters of from several hundred angstroms to microns. The fibers are composed of alligned polymer strands in crystalline form. The electronic properties are quite anisotropic due both to the microscopic structure (which gives higher conductivity along the polymer strands) and to the arrangement into fibers. Recent experiments have shown that the latter effect is dominant in causing the anisotropy. In addition $(SN)_x$ has been shown to be superconducting below 0.3K. It has extremely anisotropic critical fields resulting from the weak electronic coupling between fibers. Although the hard structure is quite three dimensional it has been suggested that the small diameter of the fibers may lead to quasi-one dimensional superconductivity in the temperature regime where the coherence length ξ (T) is large compared to the diameter. The reduced dimensionality would lead to large superconducting fluctuations above T_c.[1-4]

The conductivity of $(SN)_x$ has shown a resistivity minimum which is very sample dependent, the general feature being that "high quality samples" have less of an increase in ρ as the temperature is lowered than low quality samples. This has led some authors to discuss a Kondo effect in $(SN)_x$, especially in light of the presence of low temperature magnetic susceptibility measurements which indicate the presence of free spins.[5]

The thermopower measurements reported in this paper were undertaken in order to elucidate these questions. Thermopower is a zero current measurement so that the superconducting fluctuations can be probed in the absence of possible critical current or heating effects. Several investigations have also shown the sensitivity of thermopower to the

presence of magnetic impurities. In addition the phonon drag contribution to the thermopower indicates the dominant phonon scattering processes which can be compared with our comparison study of the thermal conductivity.

The thermopower measurements were performed in vacuum outside the mixing chamber of a dilution refrigerator. With the same setup we were also able to measure the thermal conductivity, electrical resistivity, and the upper critical field (as a function of angle and temperature) of this sample. The thermal conductivity results are presented in our companion paper.[6] The apparatus is more fully described there. Briefly, four electrical and thermal eontacts were made to an $(SN)_x$ crystal of dimensions 4.9 x 0.12 x 0.09 mm by evaporating gold contacts, wrapping 1 mil Cu wire around these contacts and applying silver past- . We have found that evaporated Au films produce the lowest contact resistance to $(SN)_x$. Heat is supplied through one of the end contacts with the opposing end connected to a temperature controlled plate which acts as the thermal ground. The temperature difference between the two inner contacts is measured with carbon resistance thermimolar. The thermoelectric voltage is measured across the same inner contacts. The Cu wires from these inner contacts are heat sunk to separate copper pads for the temperature measurements. Superconducting wire leads are used from these pads for the electrical measurements, thus the thermoelectric voltage produced is entirely generated by the thermopower of $(SN)_x$. Further evidence for the neglect of lead connections comes from the fact that no voltage is observed when the $(SN)_x$ is superconducting.

In figure 1 we have plotted the absolute thermopower as a function of temperature in the range .1K-4.2K. The sign, magnitude, and temperature

dependence of the thermopower fit fairly well onto previous measurements by several authors at $T>4.2$ temperature is increased above 4.2 these authors found an increase in S with a maximum (negative) value at ~20K. They associated this behavior with a phonon drag peak. Two of the main features of figure 1 are qualitatively well understood, the phonon drag contribution for T>1K and the superconducting transition at T = .27K. We will discuss these aspects first.

The thermopower of a metallic system is usually separated into a diffusion term S_e and a phonon drag term S_ℓ. The diffusion term probes the electronic properties of the system and is often written in the form:

(1)

where D(E) is the density of states and μ (E) is the energy dependent mobility. The phonon drag term in its simplest form becomes:

(2)

where C_e is the lattice specific heat, τ_{pe} is the electron phonon scattering time and τ_p is the phonon scattering time for all interactions except electron-phonon. Since the lattice specific heat varies as T^3 at low temperatures and $S_e \sim T$ the thermopower is often presented as

$$S = AT + BT^3 \tag{3}$$

In order to separate the two terms it is convential to plot S/T vs T^2 as we have done in figure 2 for $1 \leq T \leq 4.2$. In this temperature region we find quite good agreement with the temperature dependence of eq. 3. The T = 0 intercept indicates a very small electronic contribution. Although we do not know enough about the mobility term to make any qualitative comparison, band structure calculations have shown that $(SN)_x$ is a semi metal with a low density of states at E_F. Specific heat

measurements indicate a density of states of 0.14 states/(ev-spin molecule). However there are contributions to the thermopower from both electrons and holes and our measurements show that these contributions tend to cancel one another.

The slope obtained from figure 2 shows a large phonon drag contribution. The specific heat measurements for T<4.2K fit a T^3 temperature dependence so that the phonon spectrum is quite three dimensional in this range. From specific heat and Hall effect measurements we can calculate $\frac{C_e}{ne} = -0.040\ T^3 (\mu V/K^4)$. Between 1K and 4.2K the experimental thermopower yields $S = 0.043 \pm 0.004\ T^3\ (\mu V/K^4)$ with a negligible linear term. Looking at equation 2 one can see that the dominant phonon scattering must be from electrons in this temperature region. The value of n from Hall effect measurements (n = 3.2x10) corresponds with the value calculated taking the relative volumes of electron and hole pockets in the Fermi surface into account. If the value of n from x-ray spectra[5] is used, C_e/ne is reduced and there is no way to obtain as large a value of S as is seen experimentally. It is not possible to determine the dominant electron scattering mechanism from these measurements but it is worth pointing out that the phonon "bottleneck" rules out the electron-phonon interaction as a means of dissipating electron energy. Since phonon-phonon and phonon-impurity scattering are not dominant we would expect large phonon mean free paths as is observed in thermal conductivity measurements.[6]

We will now consider the temperature region T<1K. The dominant structure seen in this region on figure 1 is a sharp drop in the thermopower at 0.275K. We associate this behavior with the superconducting transition. The transition temperatured measured resistively on this crystal is 0.275K where we have taken the of both the S

and P drop. The width of the transition is about 50 mK from both measurements. The thermopower in the superconducting state should be zero due to the vanishing of the entropy in the condensate. To within experimental error the thermopower below T_c is zero for our sample.

In order to confirm that the reduction of the thermopower below .275K is due to superconductivity we have plotted S as function of magnetic field for T = .250K in figure 3. Since the critical fields are strongly anisotropic we have shown the dependence of S on H for fields both perpendicular and parallel to the polymer and fiber axis ($H_\perp$ and $H_\parallel$ respectively). The arrows shown on figure 3 indicate the midpoint of the superconducting transition measured resistively for $H_\parallel$ and $H_\perp$. It is clear from this figure that the thermopower shows the superconducting transition as a function of magnetic field in much the same way as the resistance does.

What is very unusual about the magnetic field dependence is that the thermopower, once the superconductivity has been quenched, is considerably higher than the thermopower observed above T_c (see figure 1). In addition we see that as the magnetic field (either $H_\perp$ or $H_\parallel$) is increased above the critical fields, the thermopower reaches a maximum and then decreases to a very low value at H = 15K gauss. Since the magnetic field behavior is isotropic for high fields we believe that we are observing spin rather then orbital effects at this low temperature. The magneto-thermopower is not merely reflecting an orbital Ettingshauser-N effect (similar to orbital magneto-resistance) which would be highly arisotropic. The magnetic field dependence of thermopower is also seen to fit a 1/H form rather than H^2.

The thermopower as a function of magnetic field has the general shape shown in figure 3 for temperatures above T_c as well as below. The significant differences are that above T_c the thermopower starts at a non zero value at zero field, increases to a maximum and then decreases to a non zero value, as the field is increased. In figure 4 we have plotted the maximum thermopower (as the field is varied) for a particular temperature as a function of temperature. The field at which this maximum occurs is shown in figure 5. From figure 4 we see that the thermopower in the normal state is increasing as the temperature is decreased.

We attribute the low temperature increase of S to the interaction of the conduction electrons with localized magnetic impurities which can be quenched by the application of a magnetic field. Note that the characteristic magnetic field needed to reduce the thermopower is of the order of 10K gauss. Taking a g value of 2 this would correspond in magnetic interaction energy to a thermal energy associated with approximately 1K which is characteristic of the temperature at which the thermopower maximum is reduced.

The increase in S with decreasing T (at temperatures below the phonon drag peak) has been observed in many conventional metallic systems with magnetic impurities and is associated with the Kondo effect. Calculations of the temperature and magnetic field dependence of the thermopower have been done. In the high temperature regime the temperature dependence is logarithmic and the field dependence is 1/H. While we do not have sufficient temperature data to compare with this dependence, we have plotted a 1/H curve in figure 3 and see reasonable agreement. In Kondo systems there is also a resistivity minimum and a negative magnetoresistance. The resistance of our $(SN)_x$ crystal is plotted as a function of temperature in figure 6.

The resistance is increasing with decreasing temperature. This behavior has been seen in many of the previous resistivity studies some of which have discussed it in terms of the Kondo effect. As a rule of thumb most authors suggest that more perfect crystals have less of a resistivity increase at low temperature[1]. Moreover, Kahlert and Seeger have observed that samples which show a positive magnetoresistance can be bent to introduce defects and when remeasured give an initial negative magnetoresistance.

The question naturally arises as to where these local moments which are clearly present from low temperature magnetic susceptibility studies, come from. One possibility, suggested by the quality and bending studies, is the localization of electrons on broken band, caused by fractures on the polymer chains. In this case the interaction of the local moments with the conduction electrons would arise via a form of superexchange.

In further investigating figure 3 we note that for a finite $h_\perp$ the thermopower is larger than for zero field even at temperatures considerably above T_c. Below T_c we associated the difference with superconductivity, largely by comparison with the magnetic field dependence of the resistance. Above T_c the situation is considerably more complicated. Civiaketal[13] have shown that the resistance difference between zero field and "using a magnetic field to quench the residual superconductivity" can be fit to an Aslamazon and Larkin expression for one dimensional fluctuations. However, they also imply that there is negligible magnetoresistance at 4.2K. Several other authors have investigated the magnetoresistance and find a variety of effects. Beyer et al.[14] report a small positive magnetoresistance, a larger negative magnetoresistance and a large positive magnetoresistance as magnetic

field is increased to 7S Kgauss. In magnetoresistance measurements from 0-15 K gauss on our sample we have found both positive and negative resistance charges from $T_c<T$ to $T\approx 2K$. For perpendicular fields the general bahavior is an initial resistance increase followed by a larger decrease. The effects are anisotropic and the interpretation at present is ambiguous.

We do not have enough data points directly above T_c to be able to compare with the theoretical treatment of Maki[15] for the fluctuation thermopower in a one dimensional superconductor. We see in figure 5, however, that the field required to maximize the thermopower has an interesting temperature behaviour. Since the field at maximum thermopower is minimum at T_c we believe this behaviour is somehow related to superconductivity.

In conclusion, from our study of the thermoelectric power of $(SN)_x$ we have learned that: 1) for $T>1K$ the phonon scattering is dominated by the electron-phonon interaction, 2) thermopower confirm the superconducting transition at ~.3K and, 3) there is strong evidence for local moments which may produce a low temperature Kondo effect. There is also some tentative evidence of superconducting fluctuations above T_c but considerably more work is needed to separate out several magneto-transport effects.

Acknowledgements

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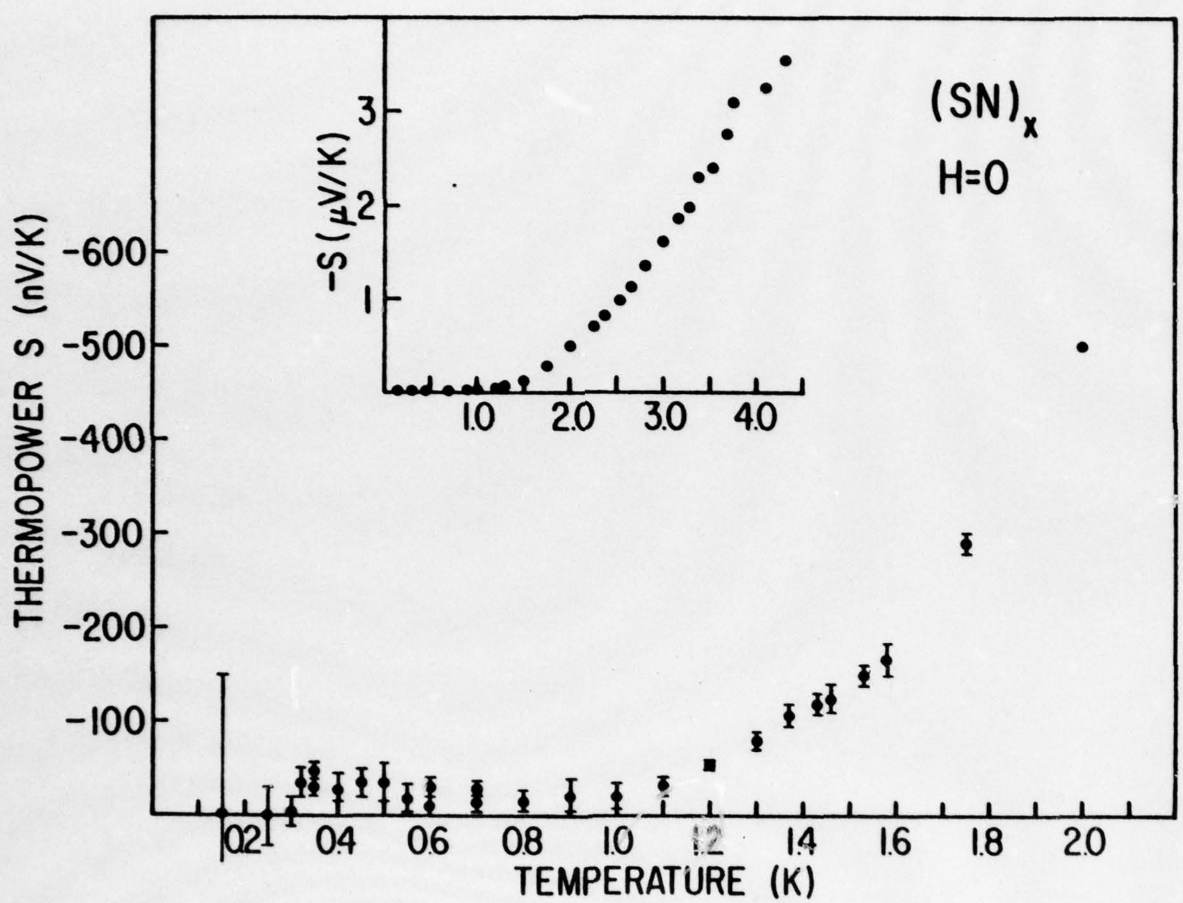
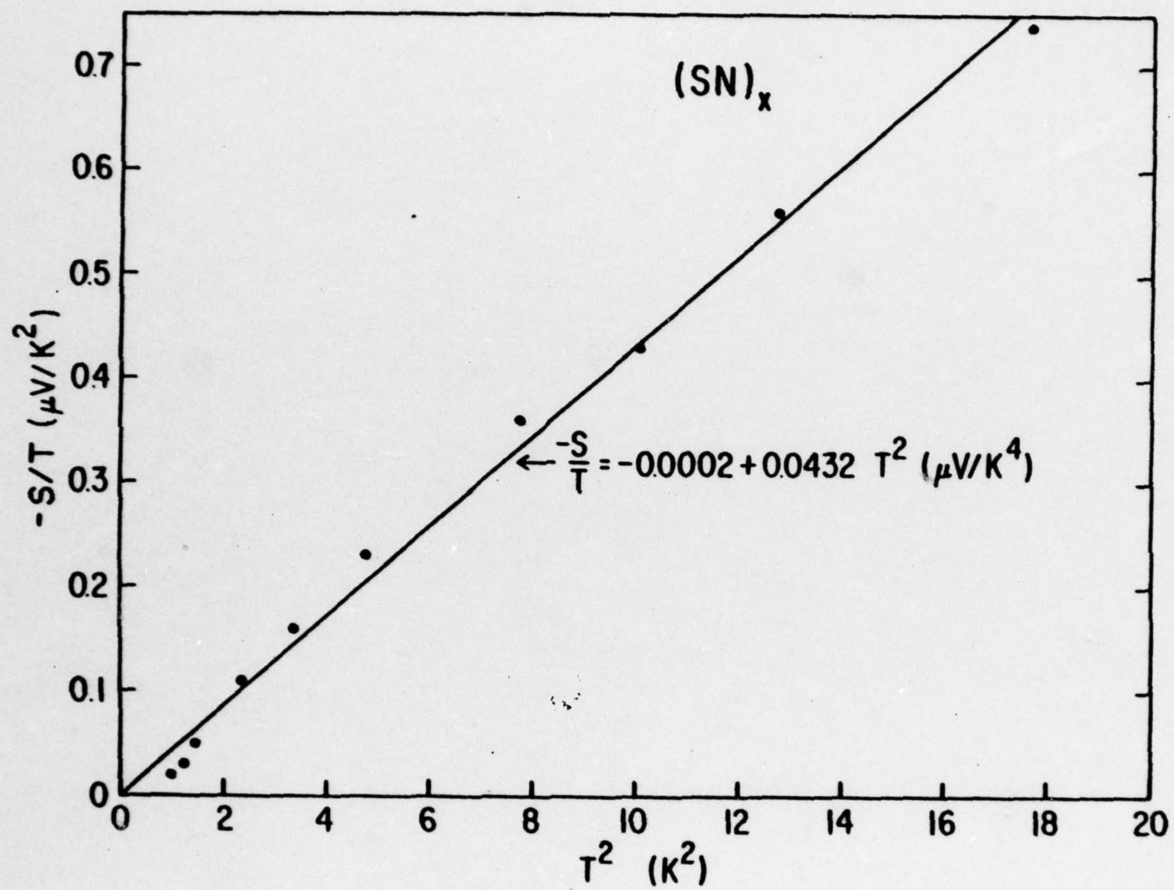
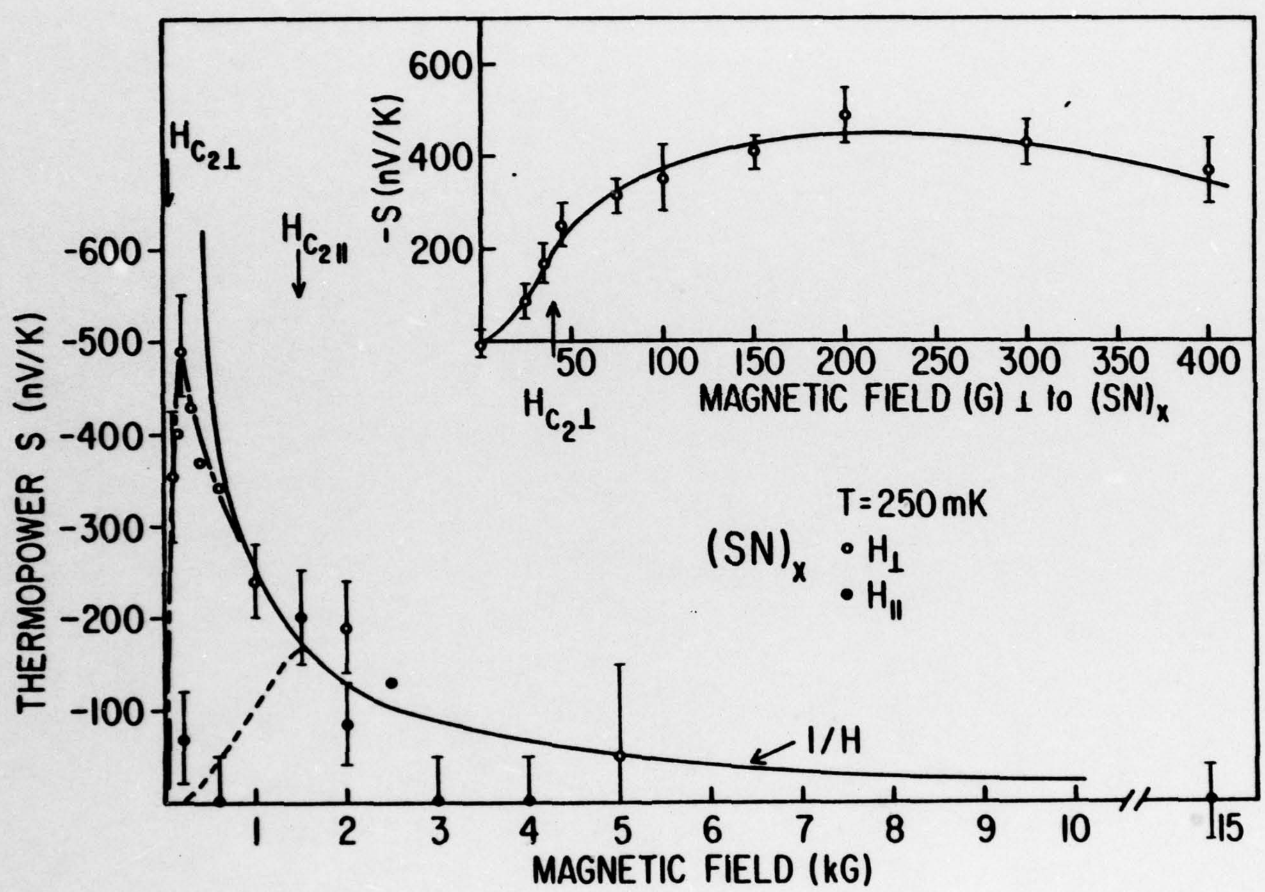
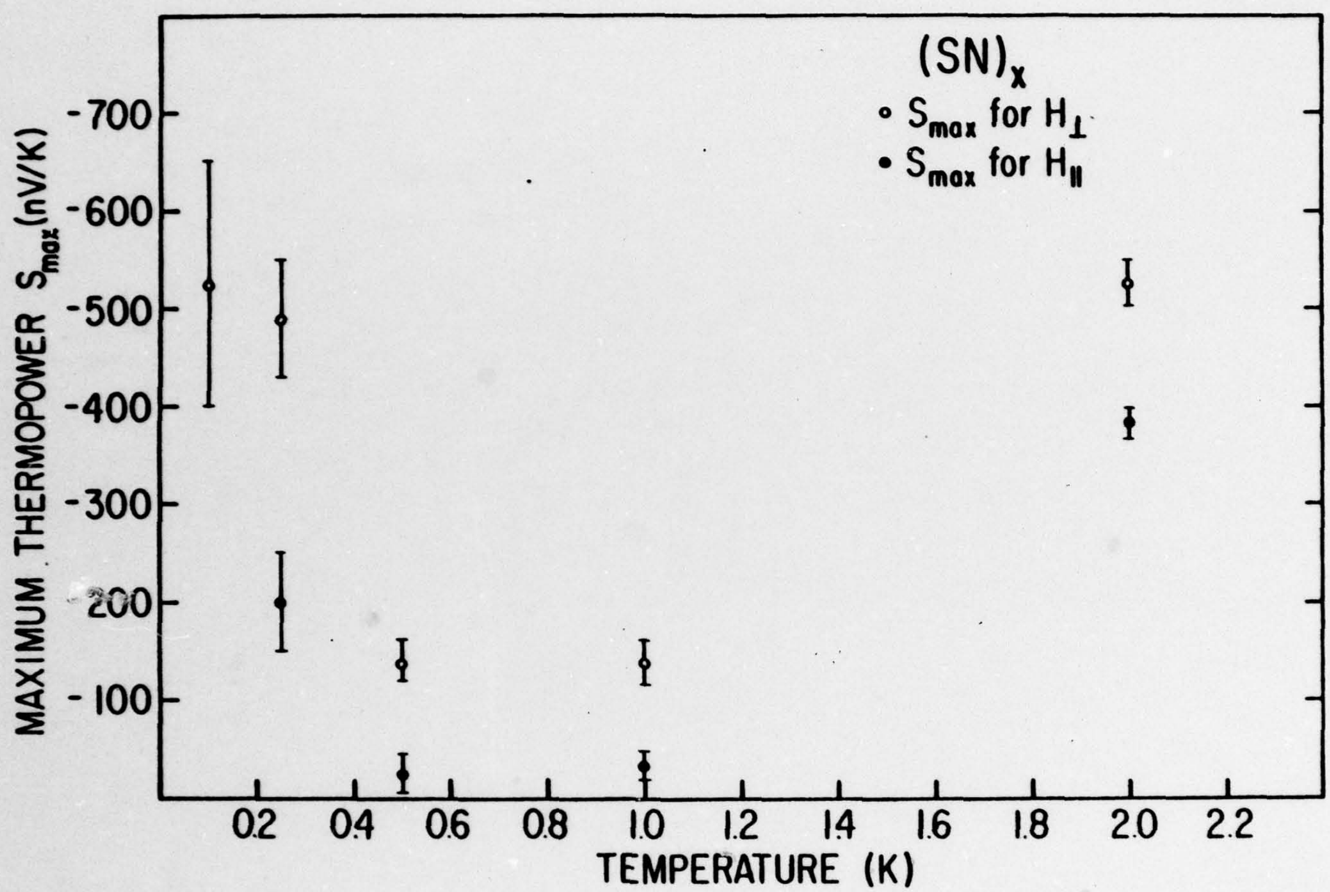
Figure Captions

1. Thermopower of $(SN)_x$ in zero magnetic field as a function of temperature.
2. Thermopower of $(SN)_x$ divided by temperature as a function of temperature squared for 1.K≤[illegible]4.2.
3. Thermopower of $(SN)_x$ at T = 250 mK as a function of magnetic field. The dotted lines and the line in the insert are guides to the eyes.
4. The maximum thermopower of $(SN)_x$ as a function of temperature for both parallel and perpendicular magnetic fields.
5. The field at which the maximum thermopower of $(SN)_x$ occurs as a function of temperature.
6. The resistance of $(SN)_x$ as a function of temperature.

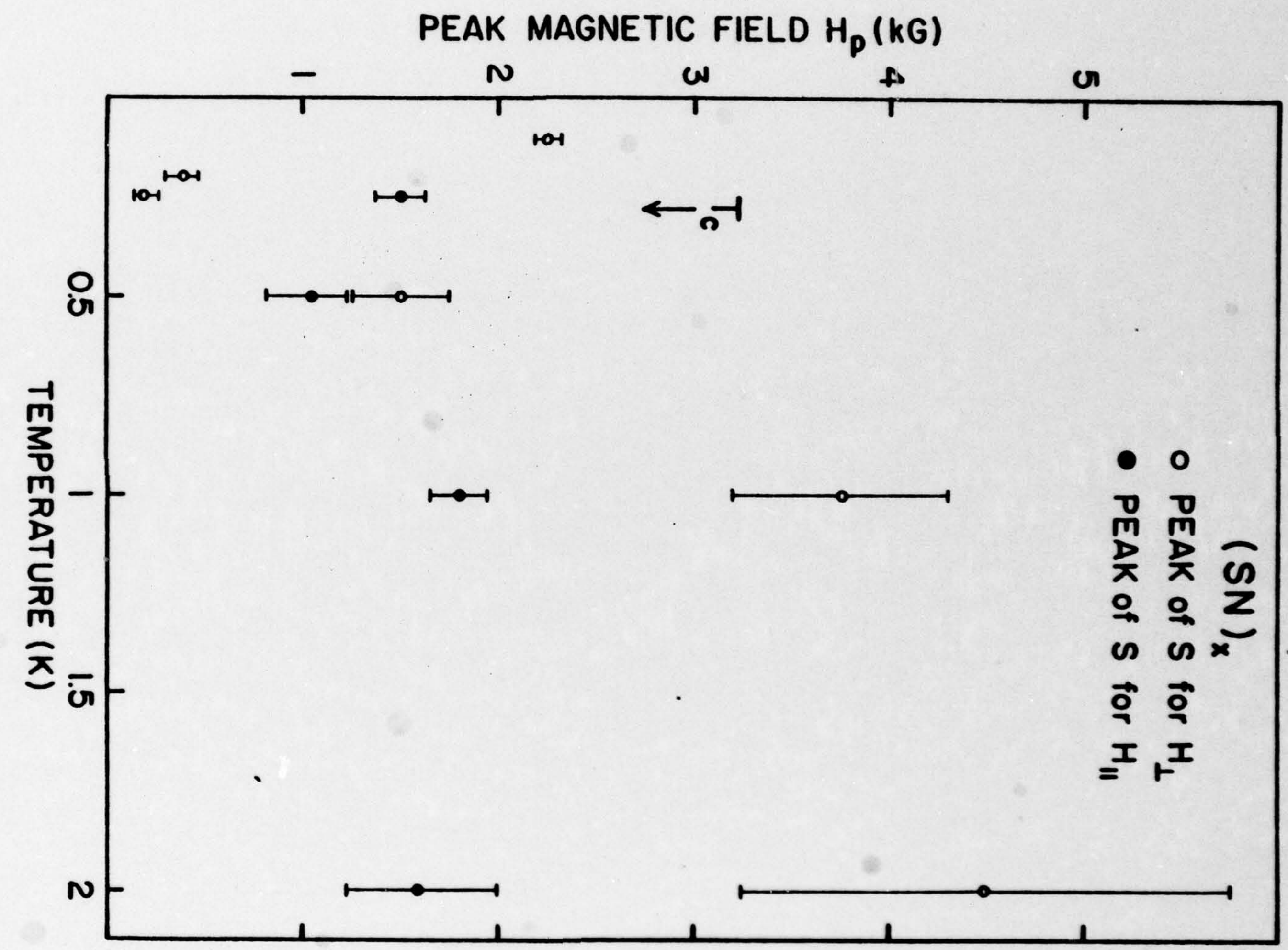

(SN)x
H=0
THERMOPOWER S (nV/K)
-600
-500
-400
-300
-200
-100
TEMPERATURE (K)
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
-S (μV/K)
3
2
1
1.0
2.0
3.0
4.0

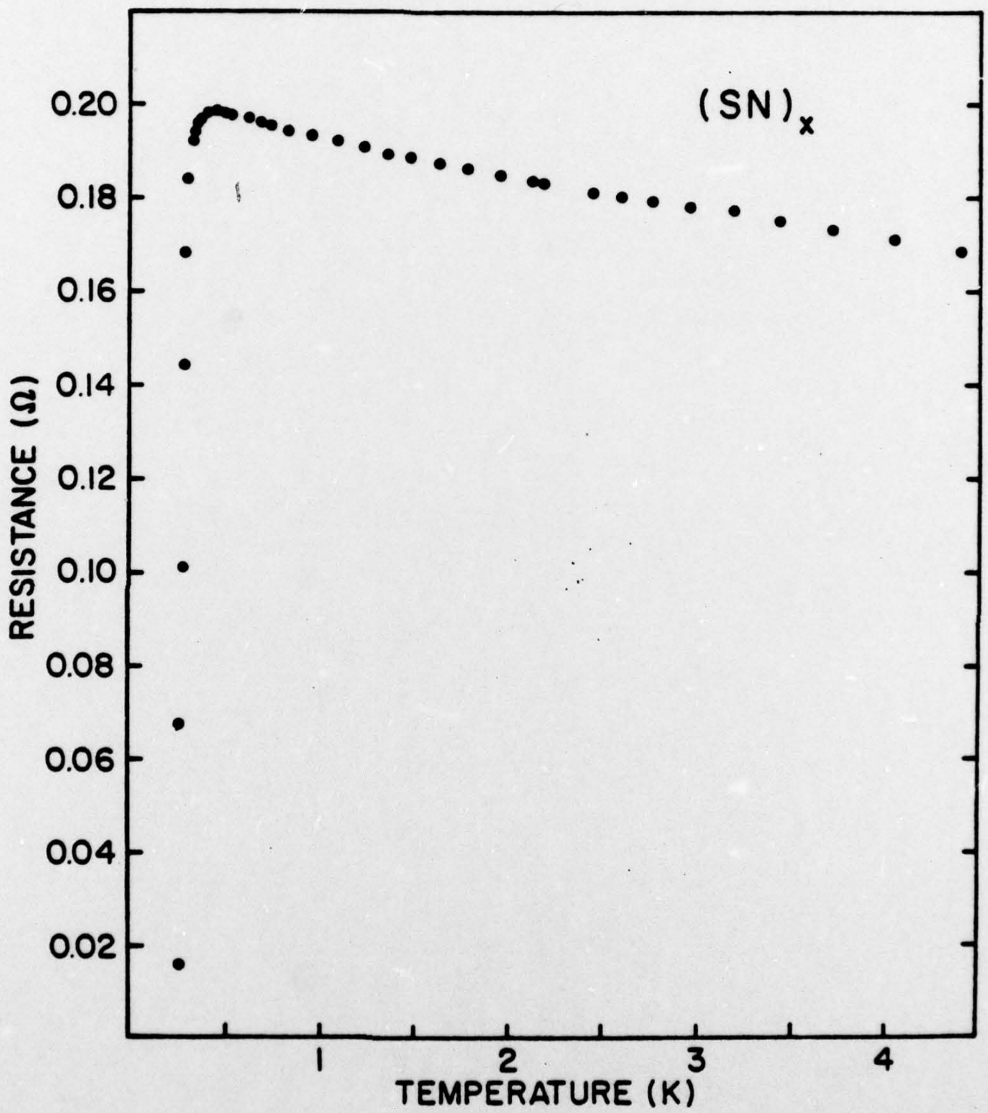

(SN)x
-S/T (μV/K2)
T2 (K2)
-S/T = -0.0002 + 0.0432 T2 (μV/K4)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
2
4
6
8
10
12
14
16
18
20


THERMOPOWER S (nV/K)
-600
-500
-400
-300
-200
-100
MAGNETIC FIELD (kG)
1
2
3
4
5
6
7
8
9
10
15
$H_{c_2\perp}$
$H_{c_2\parallel}$
1/H
T=250 mK
$(SN)_x$
$\circ$ $H_\perp$
$\bullet$ $H_\parallel$
-S (nV/K)
600
400
200
50
100
150
200
250
300
350
400
MAGNETIC FIELD (G) ⊥ to $(SN)_x$
$H_{c_2\perp}$



(SN)x
Smax for H⊥
Smax for H∥
-700
-600
-500
-400
-300
-200
-100
MAXIMUM THERMOPOWER Smax (nV/K)
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
TEMPERATURE (K)


PEAK MAGNETIC FIELD H_p (kG)
1
2
3
4
5
TEMPERATURE (K)
0.5
1
1.5
2
T_c
$(SN)_x$
○ PEAK of S for $H_\perp$
● PEAK of S for $H_\parallel$


(SN)x
RESISTANCE (Ω)
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
1
2
3
4
TEMPERATURE (K)

THERMOPOWER OF $(SN)_x$ AT LOW TEMPERATURES

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Résumé. – Nous avons mesuré le pouvoir thermoélectrique de $(SN)_x$ entre 0,1K et 4,2K. Au dessus de 1K, une importante contribution du processus de "phonon drag" a eté observée, ce qui peut etre associé a une forte interaction electron-phonon. En dessous de 1K, on obtient un comportement qui résulte de la présence, d'une part d'un effet Kondo à faible T_K, et d' autre part de la transition supraconductrice.

Abstract.– We have measured the thermoelectric power of $(SN)_x$ from 0.1K to 4.2K. A large phonon drag contribution is observed above 1K which can be associated with strong electron-phonon scattering. The superconducting transition is seen as well as a rising thermopower contribution below 1K resulting from a Kondo effect with low T_K.

The metallic polymer $(SN)_x$ has unusual low temperature transport properties [1], including a resistivity minimum, an anomalously large thermal conductivity [2] and a superconducting transition at 0.3K. In order to investigate the origin of these effects we have investigated the thermoelectric power of $(SN)_x$ in the temperature region 0.1 - 4.2K. The experiment was performed in vacuum outside the mixing chamber of a dilution refrigerator in a configuration which allowed measurements of resistance, thermal conductivity, thermopower and critical fields on the same sample.

The absolute thermopower is shown in figure 1 for zero applied magnetic field. The main features of this curve are 1) the superconducting transition at $\sim$ 0.3K where the thermopower drops to zero, 2) a small negative thermopower which decreases with increasing temperature between 0.3K and 1K and, 3) a contribution which increases rapidly with temperature above 1K. Previous thermopower measurements have been performed down to 4.2K and indicate a phonon drag peak at about 20K [3]. The present data fit onto previous measurements but gives slightly higher values. We therefore associate feature 3 above with the low temperature tail of the phonon drag peak.

The phonon drag contribution to the thermopower can approximately be written in the form [4]

$$S_\ell = \frac{C_\ell}{ne} \frac{1/\tau_{pe}}{1/\tau pe + 1/\tau P} \qquad (1)$$

Where C_ℓ is the lattice specific heat, n is the electron density, $1/\tau_{pe}$ is the electron-phonon scattering rate and $1/\tau_{pe}$ is the phonon relaxation rate due to all other processes. From specific heat and hall effect measurements we can calculate $\frac{C_\ell}{ne} = -.40\ T^3 (\mu V/K^4)$. Between 1K and 4.2K the experimental thermopower yields $S = 0.43 \pm .04 T^3$ $(\mu V/K^4)$ with a negligible linear term.

We therefore find that the phonon drag term corresponds to the phonon bath traveling with the same drift velocity as the electrons. According to equation 1 this implies that the dominant <u>phonon</u> scattering mechanism is the electron-phonon interaction. It is not possible to determine the dominant electron scattering mechanism from these measurements but it is worth pointing out that the phonon "bottleneck" rules out the electron-phonon interaction as a means of dissipating electron energy. Since phonon-phonon scattering and phonon impurity scattering are not dominant we would expect large phonon mean free paths as is observed in thermal conductivity measurements [2].

In order to demonstrate that the vanishing thermopower below 0.3K was the result of superconductivity, parallel and perpendicular magnetic fields were applied as shown in figure 2 for a sample temperature of 250mK. It is known that the critical fields of $(SN)_x$ are highly anisotropic [5]. We have shown $H_{c2\perp}$ and $H_{c2\parallel}$ as measured resistively for this sample at 250mK. The thermopower rises from zero at the characteristic fields. However two unexpected effects are observed. The maximum thermopower as $H_\perp$ is varied is more than an order of magnitude larger than what would be expected by extrapolation of the data shown in figure 1. Further, the thermopower is not independent of H for fields greater than the critical fields.

We believe these effects are to be associated with a Kondo effect arising from localized spins perhaps located on broken polymer bonds. When the thermopower is measured in a magnetic field it is an increasing function of decreasing temperature as would be expected for a Kondo system with a Kondo temperature $\leq$ 0.1K [4].

The fact that we are observing an effect associated with localized spins may be ascertained from the similarity of the magnetic field dependence of the thermopower for $H_{\parallel}$ and $H_{\perp}$ once the appropriate critical fields have been exceeded. The thermopower for a Kondo system is calculated to vary with 1/H in the limit $g\mu_B H > k_B T$. Such a dependence is approximately observed in the experiments.

A fairly complicated magnetic field dependence to the thermopower above T_c is observed and may be indicative of fluctuations preceding the superconducting transition.

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References

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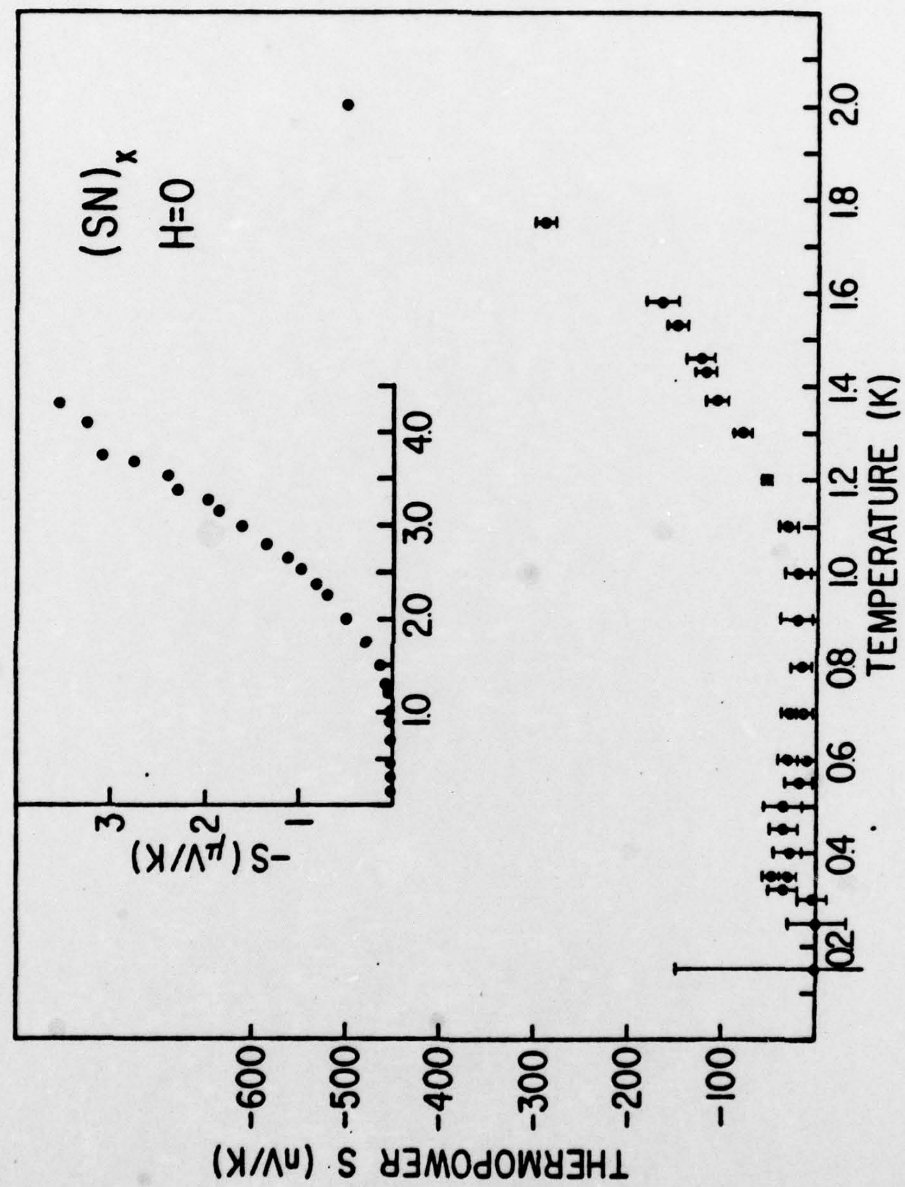
Figure Captions

Fig. 1. Thermopower of $(SN)_x$ in zero magnetic field as a function of temperature.

Fig. 2. Thermopower of $(SN)_x$ at T = 250 mK as a function of magnetic field.

Azevedo et al, Fig 1



Azevedo et al, Fig. 2